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INFLUENCE OF ELECTRODE MATERIAL ON OXYGEN OVERVOLTAGE— A THEORETICAL ANALYSIS

by

Paul Ruetschi and Paul Delahay

Report No. 18

INFLUENCE OF ELECTRODE MATERIAL ON OXYGEN OVERVOLTAGE -

A THEORETICAL ANALYSIS

by

Paul Rüetschi[1] and Paul Delahay

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ABSTRACT

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Variations of overvoltage for oxygen evolution from one metal to another primarily result from variations in the energy of the bond M-OH. The overvoltage decreases approximately in a linear manner with increasing bond energy. This relationship is verified experimentally for Ag, Au, Cd, Co, Cu, Fe, Ni, Pb, Pd, Pt, for electrolysis in 1 N potassium hydroxide at 1 amp.cm.$^{-2}$; the experimental data are those reported by Hickling and Hill. Bond energies for M-OH are calculated by three different thermodynamic cycles involving, respectively, the standard heat contents of the hydroxide, the oxide, and spectroscopic data for molecules MO. Variations of the energy of the bond M-OH, as the electrode is oxidized to a higher valence, also account for sudden breaks in plots of overvoltage against logarithm of current density. Finally, there is essentially no correlation between the oxygen overvoltage for different metals and the corresponding work functions provided that the transfer coefficient for the metals being compared is the same.

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It is well known from experimental studies that the nature of electrode material has a profound influence on the kinetics of electrode processes. The interpretation of this effect is difficult except for relatively simple reactions such as the discharge of hydrogen or hydroxyl ions. The former reaction was studied in a previous report[2], and it was shown on a theoretical basis that the overvoltage for hydrogen ion discharge varies from one metal to another primarily because of variations in the heat of adsorption of atomic hydrogen. An

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[1] Postdoctoral fellow 1953-54.

[2] P. Rüetschi and P. Delahay, Tech. Rep. to O.N.R., No 17 (1954).

interpretation of the effect of electrode material is given in this report for the electrolytic production of oxygen in alkaline aqueous solution. Unfortunately, the experimental study and the quantitative interpretation of oxygen overvoltage are far less advanced than for hydrogen overvoltage[3], but sufficient experimental data are available[4] to test an explanation of the effect of electrode material.

INITIAL AND FINAL STATES FOR HYDROXYL ION DISCHARGE

We shall assume that the discharge of hydroxyl ions can be represented by the reaction

$$M + H_2O - OH^- - e \longrightarrow M-OH + H_2O \qquad (1)$$
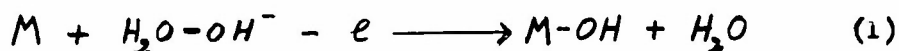
which is followed by a process yielding molecular oxygen. The nature of this process is immaterial if one assumes that reaction (1) is rate determining. This is undoubtedly the case when the overvoltage exceeds say 0.1 - 0.2 volt, i.e. when the effect of the backward electrode reaction can be neglected. As for hydrogen ion discharge[2], the overvoltage for the evolution of oxygen can be written in the form (note changes in sign)

$$\eta = \frac{RT}{\alpha F} \ln p + \frac{\Delta H^{\neq}}{\alpha \lambda F} - \left(1 - \frac{1}{\alpha \lambda}\right) \psi_0 - e_0 \qquad (2)$$

where α is the transfer coefficient for the discharge process; λ the number of hydroxyl ions which are discharged when the rate determining reaction occurs once[5]; $\Delta H^{\neq}$ the energy of activation for the discharge process; ψ_0 the difference of potential across the diffuse part of the Stern double

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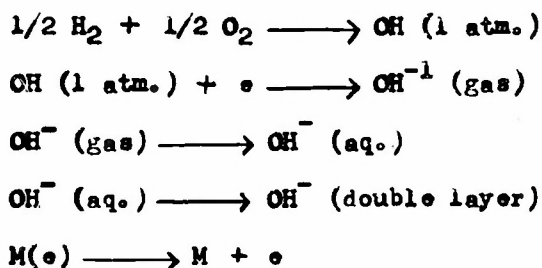[3] For a survey, see A. Hickling, Quart. Rev., 3, 95 (1949).

[4] A. Hickling and S. Hill, Discussions Faraday Soc., 1, 236 (1947).

[5] $\lambda = 1$ for hydrogen overvoltage when the discharge of hydrogen ion is the slow step.

layer at unit activity of OH⁻ ions; e_o the difference of potential from electrode to the outer Helmholtz layer at the standard reversible potential for hydroxyl ion discharge; and $\frac{p}{j}$ represents a group of terms, whose explicit form is not needed here, and which can be regarded as independent of electrode material. The quantity $\frac{p}{j}$ includes the entropy of activation for the discharge process, which will be assumed to be independent of electrode material. The derivation of equation (2) is given by Kortüm and Bockris[6] for hydrogen overvoltage. The terms $\propto$, $\Delta H^{\neq}$, and λ in equation (2) could possibly depend on the electrode material, while e_o, which includes the work function of the electrode, definitely depends on the nature of the electrode.

The interpretation of the effect of electrode material requires thus the calculation of the energy of activation $\Delta H^{\neq}$. This energy could in principle be deduced from variations of energy along the reaction coordinate. Such a method was applied by various authors[2,7,8] in the case of hydrogen ion discharge. Unfortunately, spectroscopic and other data needed in such calculations are not available for the discharge of hydroxyl ion, but useful information about factors influencing the energy of activation can be obtained by considering simply the initial and final states.

The initial state corresponds to one equivalent of hydroxyl ions in solution and the metal M from which one equivalent of electrons has been removed. The value of H_1 is obtained from the following cycle

$$1/2 \; H_2 + 1/2 \; O_2 \longrightarrow OH \; (1 \; atm.)$$

$$OH \; (1 \; atm.) + e \longrightarrow OH^{-1} \; (gas)$$

$$OH^- \; (gas) \longrightarrow OH^- \; (aq.)$$

$$OH^- \; (aq.) \longrightarrow OH^- \; (double \; layer)$$

$$M(e) \longrightarrow M + e$$

[6] G. Kortüm and J.O'M. Bockris, Textbook of Electrochemistry, vol. II, p. 430 eq. 80; note that e_o was dropped inadvertently by the authors.

[7] See references in N.K. Adam, The Physics and Chemistry of Surfaces, 3rd Ed., Oxford University Press, 1941, 331ff.

The energy corresponding to the transfer of hydroxyl ions from solution to the double layer will be assumed to be negligible. This hypothesis is justified as was shown by Parsons and Bockris[8] for the discharge of hydrogen ions. The electron affinity and the heat of hydration or hydroxyl ion are known, but the sum of these two quantities can be calculated from the following cycle
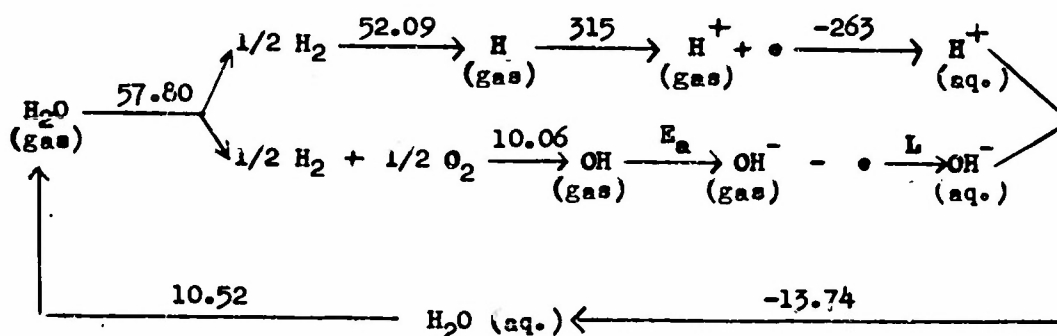
where E_a and L are the electron affinity and the heat of hydration of hydroxyl ion, respectively, and the numerical data are the changes in heat content[9]. The hydration energy of hydrogen ion, -263 kcal., is the average of two reported values, -250 kcal.[10] and -276 kcal.[11]

One deduces from this cycle that $E_a + L = -168.7$ kcal., and the heat contents for the initial state is thus (in kcal.)

$$H_i = \phi_w - 158.7 \qquad (3)$$

where ϕ_w is the electronic work function of the electrode M.

As was pointed out in a similar calculation for hydrogen ion[2], the surface

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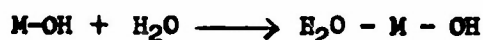8 R. Parsons and J.O'M. Bockris, Trans. Faraday Soc., 47, 914 (1951).

9 Taken from Selected Values of Chemical Thermodynamic Properties, Series 1, National Bureau of Standards, 1949.

10 W.M. Latimer, K.S. Pitzer, and C.M. Slansky, J. Chem. Phys., 7, 108 (1939).

11 J.D. Bernal and R.H. Fowler, ibid., 1, 515 (1933).

potential[12] is neglected in the writing of equation (3). This simplification introduces an error in the calculation of $\Delta H^{\neq}$ for reaction (1), but the sequence of overvoltage values is not modified if the surface potential is essentially the same for all metals. It will be assumed that this is the case.

The final state is defined as one equivalent of OH radicals bound to metal M. The corresponding heat contents H_f is derived from the cycle

$$1/2 \ H_2 + 1/2 \ O_2 \ (1 \ atm.) \longrightarrow OH \ (1 \ atm.)$$

$$OH \ (1 \ atm.) + M \longrightarrow M\text{-}OH$$

$$M\text{-}OH + H_2O \longrightarrow H_2O - M - OH$$

Thus

$$H_f = R - D(M\text{-}OH) + 10.06 \tag{4}$$

where H_f is in kcal., R is the energy of interaction between M-OH and water, D(M-OH) is the energy of the bond M-OH, and 10.06 kcal. is the heat of formation of the hydroxyl radical. The interaction energy R is not known, and we shall assume that it is independent of the electrode material. This may be a rather coarse approximation.
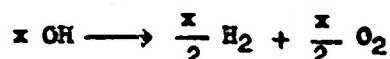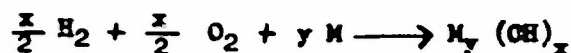
CALCULATION OF THE ENERGY OF THE M-OH BOND

The comparison of overvoltage values for different metals, i.e. the comparison of the corresponding $\Delta H^{\neq}$'s requires values of the bond energy D(M-OH) appearing in equation (4). These energies are not known, but approximate values can be obtained by the following three methods.

First Method.

From the following cycle

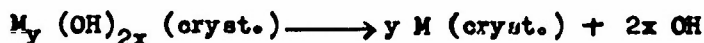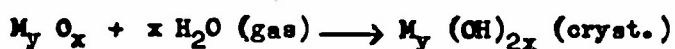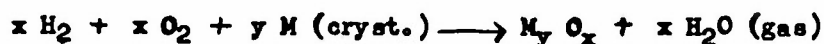[12] For references pertaining to surface potentials, see ref.2 .

$$\frac{x}{2} H_2 + \frac{x}{2} O_2 + y M \longrightarrow M_y (OH)_x$$

$$M_y (OH)_x \longrightarrow y M (cryst.) + x OH$$

$$x OH \longrightarrow \frac{x}{2} H_2 + \frac{x}{2} O_2$$

one deduces, by expressing that $\sum \Delta H^0 = 0$, the bond energy (in kcal.)

$$D(M-OH) = 10.06 - \Delta H^0 / x \tag{5}$$

where 10.06 is the energy of formation of the hydroxyl radical, and ΔH^0 is the standard energy of formation of the hydroxide.

Second Method

The cycle is

$$x H_2 + x O_2 + y M (cryst.) \longrightarrow M_y O_x + x H_2O (gas)$$

$$M_y O_x + x H_2O (gas) \longrightarrow M_y (OH)_{2x} (cryst.)$$

$$M_y (OH)_{2x} (cryst.) \longrightarrow y M (cryst.) + 2x OH$$

$$y M (cryst.) + 2x OH (gas) \longrightarrow y M (cryst.) + x H_2 + x O_2$$

and the resulting bond energy is (in kcal.)

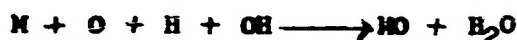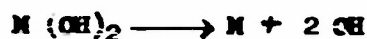$$D(M-OH) = \frac{1}{2x} \left(- x \Delta H^0_{H_2O} - \Delta H^0_{M_y O_x} + 2 \times 10.06 x \right) \tag{6}$$

on the assumption that the heat of hydration of the oxide can be neglected. This is a reasonable simplifying assumption, and the bond energy is

$$D(M-OH) = 38.96 - \Delta H^0_{M_y O_x} / 2x \tag{7}$$

Third Method

The bond energy D(M-OH) is calculated from spectroscopic data for the dissociation of the diatomic molecule M-O. The following cycle, in which all the species are in the gaseous form, is used

$$MO + H_2O \longrightarrow M(OH)_2$$

$$M(OH)_2 \longrightarrow M + 2 OH$$

$$M + 2 OH \longrightarrow M + O + H + OH$$

$$M + O + H + OH \longrightarrow MO + H_2O$$

The corresponding bond energy $D(M-OH)$ is (in kcal.)

$$D\left(M-OH\right) = \frac{1}{2}\left[D\left(M-O\right) + D\left(O-OH\right) - D\left(O-H\right)\right] \qquad (8)$$

if one neglects the heat of hydration of the oxide (see second method).
One has (in kcal.)

$$D\ (H-OH) = 52.09 + 10.06 + 57.80$$

$$D\ (O-H) = 52.09 + 59.16 - 10.06$$

where 52.09 is one-half of the heat of dissociation of H_2, 10.06 the energy
of formation of the hydroxyl radical, 57.80 the standard energy of formation
of water, and 59.16 the standard energy of formation of hydroxyl ion. Thus

$$D\left(M-OH\right) = \frac{1}{2}\left[D\left(M-O\right) + 18.76\right] \qquad (9)$$

The value of $D(M-OH)$ for silver cannot be calculated either by the
first method because the heat of formation of the hydroxide is not known,
nor by the second method because silver atoms are associated in the oxides
(Ag_2O, Ag_2O_2). The third method was modified, and the following cycle was
used

$$M + 2 OH \longrightarrow MOH + OH$$

$$MOH + OH \longrightarrow MO + H_2O$$
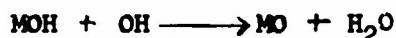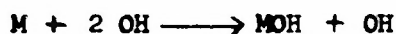
where all the species are in the gaseous form.

Bond energies calculated by the above three methods are listed in
Table I. Thermodynamic data were taken from the Bureau of Standards Tables[9].

and spectroscopic data are from Herzberg[13] and Gaydon[14]. It is to be noted that the bond energy may vary markedly with the oxidation number. Thus D(M-OH) calculated by the first method is 74.3 kcal. for $Ni(OH)_2$ and 64.1 kcal. for $Ni(OH)_3$. Likewise, one calculates by the second method values of D(M-OH) of 66.2 kcal., 62.0 kcal., and 56.5 kcal. from Pb O, $Pb_3 O_4$, and $Pb O_2$, respectively. Generally, the higher is the oxidation number, the lower the bond energy.

OVERVOLTAGE VERSUS ENERGY OF THE BOND D(M-OH)

If one assumes that $\propto \lambda$ is the same for two metals 1 and 2, the difference in overvoltage for identical conditions of electrolysis is in view of equation (2)

$$ \eta_1 - \eta_2 = \frac{1}{\propto \lambda F} \left(\Delta H_1^{\neq} - \Delta H_2^{\neq} \right) - \left[(e_0)_1 - (e_0)_2 \right] \qquad (10) $$

The quantity $\left[(e_0)_1 - (e_0)_2 \right]$ in (10) is equal to the difference of the work functions $(\emptyset_w)_2 - (\emptyset)_1$. The term in $\left(\Delta H_1^{\neq} - \Delta H_2^{\neq} \right)$ in (10) also contains the difference $(\emptyset)_1 - (\emptyset)_2$ (see equation (3)), but the difference between the work functions should be multiplied by the product $\propto \lambda$ in view of the definition of the transfer coefficient $\propto$. As a result, the difference between the $\emptyset_w$'s in (10) cancels, and <u>the difference in overvoltage for two metals is independent of the difference between the work functions of these metals.</u> This conclusion is valid provided that the mechanism of the electrode reaction is the same for metals 1 and 2 and that the transfer coefficient is also the same for the two metals. However, a small

[13] G. Herzberg, <u>Molecular Spectra and Molecular Structure</u>, Van Nostrand, New York, 2nd Ed., 1950.

[14] A.G. Gaydon, <u>Dissociation Energies</u>, Chapman and Hall, London, 1953.

difference between the α's would be unimportant.

The difference between the energies of activation in equation (10) depends on the difference between the bond energies D(M-OH) and the interaction energies between M-OH and water (see equation (4)). As D(M-OH) increases, the energy of activation decreases and the Morse curve for the energy D(M-OH) becomes steeper. Furthermore, the distance between the initial and final states along the reaction coordinate varies from one metal to another. Since the Morse curves cannot be calculated with the data now available, no detailed analysis similar to the one made for hydrogen ion[2] can be made[15]. However, the combination of these effect is such that the very _approximate_ relationship

$$\Delta H_1^{\neq} - \Delta H_2^{\neq} \approx D(M_2 - OH) - D(M_1 - OH) \qquad (11)$$

holds. This can be seen from the plot of overvoltage against D(M-OH) in Fig.1. Overvoltage values were taken from the paper of Hickling and Hill[4], and bond energies are from Table I. Values of D(M-OH) calculated by the above three methods are indicated for some metals to show the uncertainty on the energy data. The lowest values of bond energies, which often corresponds to the highest oxidation number of the metal, are generally to be prefered. This is because oxygen is evolved at very positive potentials (about 1 to 1.5 volts vs. N.H.E.) at the current density of 1 amp.cm.$^{-2}$ corresponding to the data of Fig.1. At such high pH's (1 N potassium hydroxide), the metals of Fig.1 are generally in their highest oxidation state.

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[15] The semi-empirical method of J.O. Hirschfelder, (J. Chem. Phys., 9, 645 (1941)) could be applied, but the resulting analysis does not go beyond the above approach. Hirschfelder's method was applied to hydrogen recombination at electrodes by K.E. Shuler and K.J. Laidler (J. Chem. Phys., 17, 1212 (1949)) and to hydrogen ion discharge by R. Parsons (Z. Elektrochem., 55, 111 (1951)).

Some values of the bond energies have not been plotted in Fig.1 for the following reasons. The bond energy of 71.6 kcal. for Pb obtained by the first method was not used because this datum corresponds to Pb(II) while lead is undoubtedly in the $+\not{p}$ state at the potentials corresponding to Fig.1. The values of 53.7 kcal. for Pt and 64.1 kcal. for Ni were not plotted for the same reason. The values of D(M-OH) obtained for iron by the first two methods were not used because they are higher than the value deduced from the third method. Finally, the value of 54.4 for cadmium was plotted because the values calculated by the first two methods are probably too high (by perhaps 20 kcal.).

Despite the uncertainty on the bond energies, the foregoing considera-tions show that differences in the energy of the bond M-OH essentially account for variations of oxygen overvoltage from one metal to another under given conditions of electrolysis.

In view of equations (10) and (11) the slope of the overvoltage vers-s bond energy line should be $-1/\alpha\lambda F$. Fig.1 yields the value $\alpha\lambda = 0.98$. This is of course only a very approximate value, but it agrees well with the experimental values of 1.0 one deduces from experimental plots of overvoltage versus logarithm of current density. The latter plots yield straight lines provided that $\alpha\lambda$ does not vary with current density and that there is no change in the mechanism of the electrode process as the current is varied. The slope of this line is $b = 2.3\,RT/\alpha\lambda F$ or $b = 0.059/\alpha\lambda$ at 25° if decimal logarithms are used. The experimental slopes for Co, Fe, and Cu are virtually 0.059 at 1 amp.cm.$^{-2}$, and consequently $\alpha\lambda$ is very close to unity, which is precisely the value deduced from Fig.1. The slopes b for Ag, Ni, and Pd at 1 amp.cm.$^{-2}$ are 0.15, 0.15 and 0.13, respectively (Fig.2). The corresponding overvoltages for a slope of $b = 0.059$ would be a few tenths of a volt lower, but this hardly changes the general trend of Fig.1. These

changes in slope probably result from the oxidation of the electrode to a
higher valence as will be shown below.

ENERGY OF THE BOND M-OH AND ANOMALIES IN OVERVOLTAGE
VERSUS LOG i PLOTS

The dependence of the overvoltage on the energy of the bond M-OH also
explains anomalies observed in plots of overvoltage against logarithm of
current density. Fig.2, which was constructed from data of Hickling and Hill[4],
shows such anomalies for silver, palladium, and gold. The η vs. log i plots
are composed of several linear segments with sudden variations of overvoltage.
The slope of these segments may be the same (Au) or it may vary (Ag, Pd).
For some metals such as cobalt the plot of η vs. log i yields a straight
line over a wide range of current densities.

These sudden variations in overvoltage probably result from variations
of the energy of the bond M-OH as the electrode is oxidized to a higher valence.
This view is strongly supported by the fact that the sudden increases in over-
voltage occur in the immediate vicinity of the equilibrium potentials for dif-
ferent oxidation states of the electrode. This is shown in Fig.2 for palla-
dium and gold[16]. In the case of silver a change in mechanism is primarily
observed and λ varies from 2 to 1. No break is observed in the η vs.
log i plot/ for cobalt because this metal is in his highest oxidation state at the
potentials of Fig.2.

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[16] Equilibrium potentials taken from W.M. Latimer, The Oxidation States of
the Elements and their Potentials in Aqueous Solutions, 2nd Ed. Prentice-
Hall, New York, 1952, and G. Charlot, Théorie et Méthode Nouvelle d'Ana-
lyse Qualitative, 3rd Ed., Masson, Paris, 1949.

CONCLUSION

Variations of oxygen overvoltage from one metal to another under given conditions of electrolysis in aqueous alkaline solution primarily result from variations of the energy of the bond M-OH. Variations in this bond energy as the electrode is oxidized to a higher valence account for breaks observed in plots of overvoltage against the logarithm of current density.

ACKNOWLEDGMENT

TABLE I

BOND ENERGIES AND PERTAINING DATA

Metal	1st method			2nd method			3rd method		
	H^o(*)	x	D(M-OH)	H^o(**)	x	D(M-OH)	D(***)	x	D(M-OH)
Ag	-	-	-	-	-	-	41.5	1	60
Au	100.0	3	43.4	-9.65	3	35.8	-	-	-
Cd	133.3	2	76.8	60.8	2	69.4	88	2	53
Co	176.6	3	69.0	68.0	8/3	64.5	-	-	-
Cu	106.1	2	63.2	37.1	2	57.5	113	2	66
Fe	197.0	3	75.7	63.7	3	71.8	110	2	65
Ni	162.1	3	64.1	58.4	4	53.8	100	2	59
Pb	123.0	2	71.6	66.1	4	55.5	99	2	59
Pd	169.4	4	52.4	20.4	2	49.2	-	-	-
Pt	87.2	2	53.7	13.6	8/3	44.1	-	-	-

(*) Negative heat of formation of the hydroxide of valence x in kcal./mol. at 298.1°,

(**) Negative heat of formation of the oxide of valence x in kcal./mol. at 298.1°.

(***) Spectroscopic heats of dissociation of M-O in kcal./mol.

LIST OF FIGURES

Fig.1. Oxygen overvoltage against energy of the bond M-OH. Electrolysis at 25° in 1 N potassium hydroxide and at 1 amp.cm.$^{-2}$

Fig.2. Overvoltage against decimal logarithm of current density. Experimental data taken from Hickling and Hill[4].
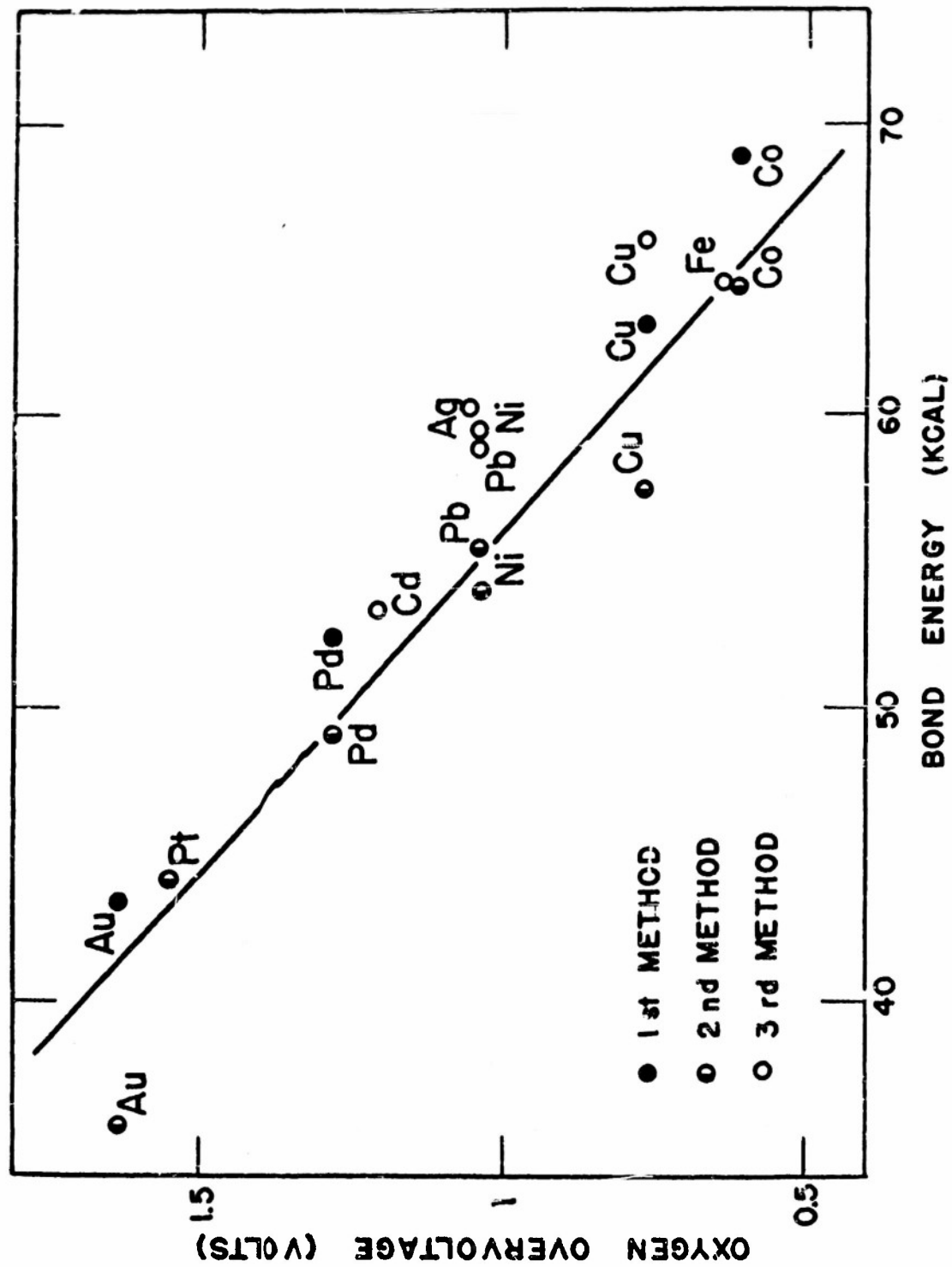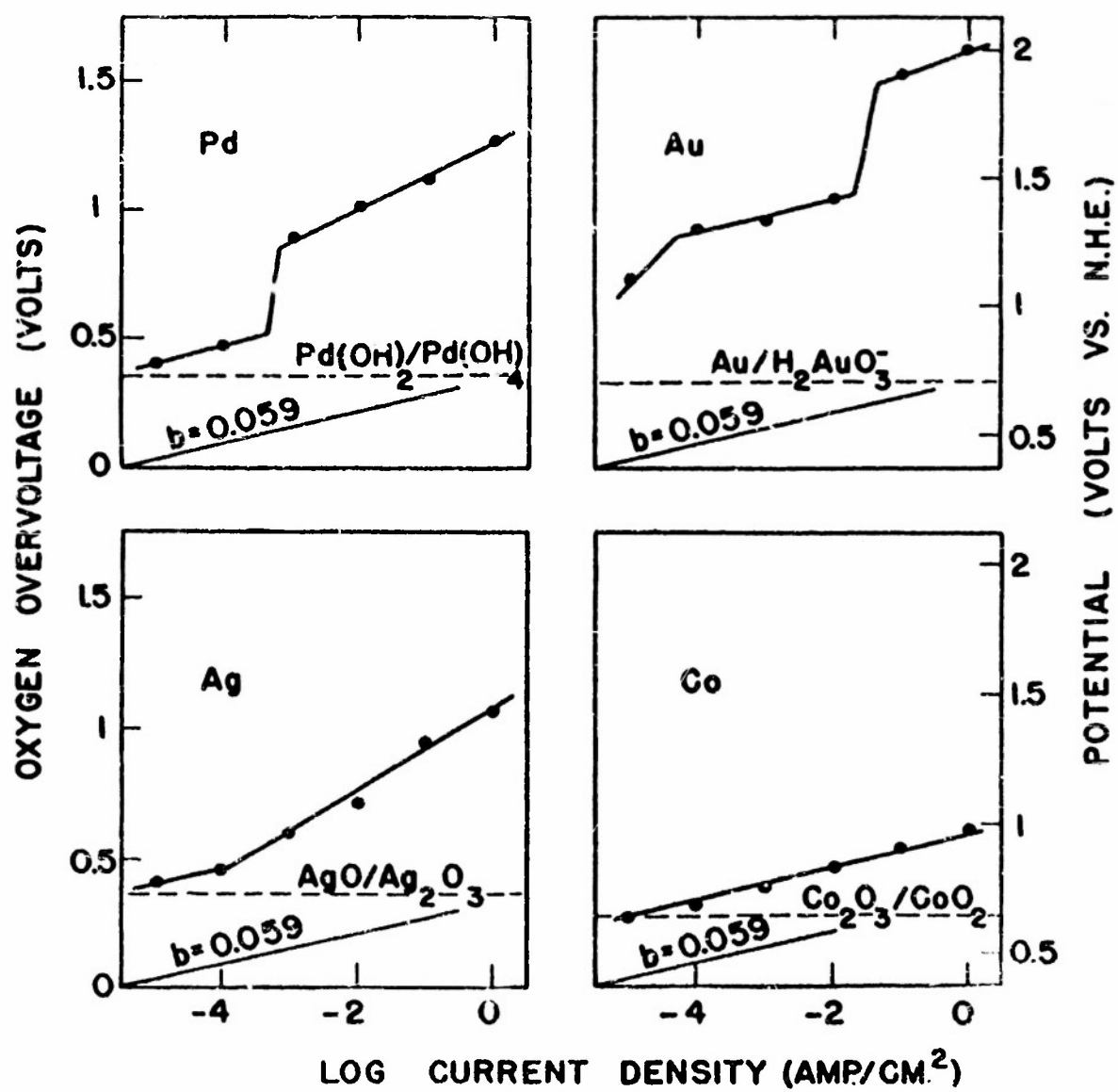
FIG. 1

FIG. 2

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